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**INHIBITION OF COKE FORMATION
DURING PYROLYSIS OF
HYDROCARBONS**

*A Thesis Submitted
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY*

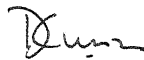
by
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to the
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

April 1997

CERTIFICATE

It is certified that the work contained in the thesis titled **Inhibition of Coke Formation during Pyrolysis of Hydrocarbons**, by **Sudip Porel**, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.



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ABSTRACT

The effectiveness of different potassium salts and calcium acetate as inhibitors for coke deposition was studied at 1073K and atmospheric pressure with ethane or naphtha as feedstocks. Potassium carbonate and another potassium salt of a weak acid (KA) were found to be effective in reducing coke formation during ethane pyrolysis. Using these additives at a concentration of 150 ppm of potassium in the feed water, a reduction of 82-88% in the coke deposition during ethane pyrolysis could be achieved due to the enhanced rates of the coke-steam reaction. However, the ethylene yields were lower and the amount of carbon oxides liberated higher as compared to a run without any additive. In comparison with potassium carbonate, the ethylene yields were higher and the yield of carbon oxides lower with KA, presumably due to the catalytic effect of potassium carbonate on the ethylene-steam reaction. The other potassium salts tested (potassium hydroxide and potassium dihydrogen phosphate) adversely affected the coke formation.

Preliminary runs conducted using potassium carbonate and potassium peroxodisulfate as additives showed that these compounds were effective in reducing the coke formation during naphtha pyrolysis. Due to the presence of sulfur in the compound itself, potassium peroxodisulfate produced lower carbon monoxide. However, the carbon oxides yields were higher with potassium carbonate. There was a 72% reduction in coke formation with potassium peroxodisulfate as compared to 28% reduction by potassium carbonate, when the same concentration (300 ppm) of both the additives were added.

Chapter 1

INTRODUCTION

In the petrochemical industry, pyrolysis of hydrocarbons using steam as an inert diluent is a very important process for the production of light olefins such as ethylene, propylene and butadiene. Steam is used to reduce the partial pressure of the hydrocarbon, resulting in higher yields of ethylene and lower coke deposition. Pyrolysis operation is conducted at high temperatures ranging from 1073K to 1123K. A common problem associated with any pyrolysis process is the deposition of coke on the inner walls of the reactor and downstream heat-exchangers. The coke layer gradually builds up and hampers the heat transfer between the furnace and the reacting process gas, and also increases the pressure drop across the reactor. In order to compensate for this, the tube metal temperature as well as the inlet reactor pressure have to be gradually increased. After a few weeks of operation, the inlet pressure or the tube metal temperature reaches the maximum allowable level, and the furnace has to be shut down for decoking. Depending upon furnace coil design, feedstocks, cracking severity and other operating parameters, the run lengths are generally limited from 30 to 70 days. Frequent decoking operations result in the loss of the production, affect coil life and increase utility costs. Coke is corrosive and can cause metallurgical failure of the reactor.

Although coke formation during hydrocarbon pyrolysis has been investigated by several workers (Sundaram et al., 1981; Albright and Marek, 1988; Froment, 1990; Reyneirs et al., 1994), the detailed coke mechanism is still not clear. Kinney and Del Bel (1954) suggested that coke is formed from a step-wise condensation of aromatic rings. Virk et al. (1974) proposed that coke formation occurs from aromatic compounds.

Very little attention has been focussed on finding methods to reduce coke formation during pyrolysis. A common method used industrially to reduce coke formation is either by addition of sulfur compounds to the feed or by presulfiding the reactor to form a passivating metal film. However, the disadvantage of using sulfur to reduce coke formation is the resultant high level of sulfur in the product, which is undesirable. Moreover, there are some studies which suggest that sulfur can catalyze coke formation (Trimm and Turner, 1981; Reyneirs and Froment, 1995). Other techniques for reducing coke formation include the addition of phosphorus compounds or passivation of the reactor walls with a layer of silica. In all the above methods, no attempt is made to gasify the coke. Some patented information (Forester, 1989; Forester, 1990; Forester, 1991; Reid and Fields, 1992; Gandman and Hong, 1994) reveal that alkali metal as well as alkaline earth metal salts can reduce coke deposition by catalyzing the coke-steam reactions. However, no details have been reported.

The objective of this study was to investigate the effectiveness of different alkali metal and alkaline earth metal salts as catalysts for the coke-steam reactions during pyrolysis. For most of the runs, the feedstock was ethane; however some runs were also made using naphtha as the feed.

Chapter 2

LITERATURE REVIEW

Although several workers have studied coke formation during pyrolysis, the exact mechanism of coke formation is still not clear. Three mechanisms can contribute to coke formation viz. (i) heterogeneous catalytic mechanism, (ii) heterogeneous non-catalytic mechanism and (iii) homogeneous non-catalytic mechanism. Coke formation by the heterogeneous catalytic mechanism involves surface reactions, diffusion and precipitation of carbon. Transition metals such as iron, nickel and chromium are known to catalyze coke formation (Albright and Marek, 1988; Reyneirs and Froment, 1995). Initially a hydrocarbon from the gas phase is adsorbed on the metal crystallite to form an organometallic complex. This complex then decomposes and yields coke on the inner metal surface. The carbon migrates through the metal surface by diffusion and deposits at the grain boundaries. Bianchini and Lund (1989) concluded that the difference in the thermodynamic activity between the carbon at the metal surface and the carbon at the grain boundaries is the driving force for diffusion. This precipitated carbon creates stresses in the metal boundary. As more carbon deposits, a carbon filament, carrying a metal particle on top of it, is formed. The filament formation was illustrated by Baker et al. (1972,1973) by means of in situ electron microscopy. The mechanism is important in the initial stages of the run when the bare metal is exposed to

the gas stream. Gradually, the metal is encapsulated with the deposited coke and the contribution of this mechanism decreases with run time. The second mechanism i.e. the heterogeneous non-catalytic mechanism is the most important source of coke during the thermal cracking of hydrocarbons. This operates over the entire run length. Here the coke consists of different layers. The growth occurs from the coke-gas interface (Ranzi et al., 1985). The coke forms due to the reaction of the precursors in the gas phase with the active sites on the surface. The important coke precursors are radicals, unsaturated molecules like ethylene, acetylene, butadiene and aromatics. Kopinke et al. (1993) observed that there are no differences in the relative constants for coke formation from a particular hydrocarbon on different material surfaces. The active sites are radical in nature and located in the coke matrix. These sites are generated due to the abstraction of hydrogen from the partially dehydrogenated carbon layer by means of small active radicals like hydrogen, methyl. The coke layer grows by the addition of unsaturated radicals and also by the reaction with radicals from the gas phase. The homogeneous non-catalytic mechanism of coke formation implies the formation of polynuclear aromatics in the gas phase due to free radical reactions. These molecules grow in the gas phase to form tar droplets which can be liquid or solid at the prevailing temperature. The tar droplets are the precursor for a part of the non-catalytic coke. Another part impinge on the wall. Those that adhere to the surface are converted to coke by dehydrogenation reactions. The tar droplets form in the gas phase by condensation reactions (Lahay et al., 1977). Bennett and Price (1981) observed the droplets hitting the solid surface by using an electron microscope. This mechanism is important only in the cracking of heavy liquid feed stocks.

Very few studies have been published on coke formation during ethane pyrolysis. Albright and co-workers (Dunkleman and Albright, 1976; Albright and McConnell, 1978) studied the rate of coke formation during ethane pyrolysis and observed that the coking rate was affected appreciably by the material of construction and the pretreatment given to the reactor. They reported an activation energy of coke formation of 250 to 290 MJ/kmol. The high initial coking rates and the carbon monoxide yields were interpreted as being associated with the catalytic activity of the wall. The carbon monoxide was mainly generated through steam reforming and implied catalytic wall effects. Sundaram et al. (1981) designed a jet-stirred completely mixed reactor to determine the main pyrolysis reaction and the kinetics of coking simultaneously. The amount of coke deposited with time was continuously measured using an electrobalance. They showed that the initial coking rate was high but gradually decreased to an asymptotic value. The asymptotic coking rate was attained when the metal particles were covered with layer of coke. Valenyi et al. (1991) indicated a shift in the controlling mechanism from heterogeneous to homogeneous carbon formation in Inconel 600 reactor during ethane pyrolysis. They used Inconel 600 and reactors and found that the latter produced little carbon deposition during ethane pyrolysis as compared to the former. The radical velocity and temperature distributions showed significant effects on carbon deposition in Inconel 600 reactors. This effect was not important in case of α -SiC reactors as the reactor wall was non-catalytic.

Very limited data is available on coke formation during naphtha pyrolysis. Newsome and Leftin (1979) reported the rates of coke formation during naphtha pyrolysis in a tubular reactor. The coking rates were found to depend on run time, inlet steam, hydrocarbon partial

pressure and temperature. Surface to volume ratio had no effect on the specific rate of coking. Kumar and Kunzru (1985) utilized the data obtained in a mixed reactor to develop a model for the coke formation in naphtha pyrolysis. Sahu and Kunzru (1988) studied the effect of material of construction on the coking rate for SS 304, SS 316 and Inconel 600 and found the asymptotic coking rate to be the lowest on Inconel 600.

Since coking is a common problem in the petrochemical industry, several studies have been made to reduce coke formation either by passivation or by gasification techniques. A technique commonly used to reduce coke formation is to either presulfide the reactor (Shah et al., 1976; Trimm and Turner, 1981) or to add sulfur compounds to the feed (Bajus et al., 1981,1983; Sahu and Kunzru, 1988). Bajus et al. (1981,1983) reported an appreciable reduction in the coking rates by using thiophene, dibenzyl sulfide or dibenzyl disulfide as additives during the steam cracking of heptane. Sahu and Kunzru (1988) studied the effect of thiophene on coking during naphtha pyrolysis and observed significant reduction in coking. However, there is some controversy regarding the effect of sulfur compounds on the coke formation. The detrimental effect of sulfur was observed at high temperatures above 1073K by an increase in coke formation on Inconel 600 reactor. This was reported by Trimm and Turner (1981). Reyneirs and Froment (1995) reported that sulfur compounds increase coke formation. They postulated that the sulfur compounds decompose at high temperature to form hydrogen sulfide. The SH radicals originating from the reaction of the gas phase radicals with hydrogen sulfide can influence the radical reactions of the heterogeneous catalytic mechanism and enhance its activity towards gas phase components.

Investigations have shown that phosphorus containing additives can significantly reduce the coking rates. Naberezhnova et al. (1983) found that organophosphorus compounds like $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{PhPS}(\text{C}_2\text{H}_5)$ and $\text{CCH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{PhPS}(\text{OC}_2\text{H}_5)$ were very effective in reducing coke formation. Phosphorus based antifoulants (Nalco 5210, 5211) have been developed by Nalco Co. (Boone, 1983) and Amoco Chemical Co. (Taylor and Allen, 1994). Ghosh and Kunzru (1988) reported a significant reduction in coking rate by adding triethyl phosphite (TEP) to the feed during naphtha pyrolysis. Vaish and Kunzru (1989) used triphenyl phosphite (TPP) and found to be even more effective than TEP. Das et al. (1992) studied the effect of benzyl diethyl phosphite (BDP) and triphenyl phosphine sulfide on coking and found BDP to be more effective than TPP.

Some investigations were also done by coating the surface of the reactor with silica. Brown et al. (1982) deposited a layer of silica coating on the internal surfaces of high alloy steel tubing at 973K to 1073K by chemical vapor deposition (CVD) of an alkoxysilane in a steam carrier gas. The silica coating was found to protect the steel surface from the oxidative attack at high temperature. Kukes et al. (1984) patented a process for coke reduction by treating hexachlorodisilane on Inconel 800.

Another method which has been used for surface passivation is Alonizing. High nickel alloys were treated with aluminium vapors at high temperature. Aluminium diffuses into the surface resulting in a protective aluminized surface. This is reputed to reduce coke formation in ethylene furnaces (Albright and McGill, 1987).

The other technique for reducing coke formation is to enhance the coke-steam reaction by suitable additives in the feed. Potassium carbonate is known to be an effective catalyst for

carbon gasification. Esso Research and Engineering Co. was issued US Patent No. 2,893,941 in 1959. In this patent potassium carbonate was added as an aqueous solution and was found to significantly reduce coke deposition during hydrocarbon pyrolysis. Mandal and Kunzru (1986) found that the rate of coke formation was significantly reduced on potassium carbonate coated stainless steel surfaces during hexane pyrolysis. Similar results were obtained by Bahadur et al. (1987) for the pyrolysis of naphtha.

Forester (1989) claimed a significant reduction of coke on stainless steel surfaces by using magnesium acetate, magnesium nitrate, calcium acetate, calcium nitrate, calcium chloride or magnesium chloride as additives in the temperature range of 1033K to 1393K. Forester (1990) discussed methods for inhibiting coke formation. The method comprised of adding rare earth element or a rare earth containing compound to the feed. Rare earth element or compound was elemental cerium or a cerium containing compound, elemental lanthanum or lanthanum containing compound. Cerium containing compounds include cerous nitrate hexahydrate, cerium oxide and ceric ammonium nitrate. Lanthanum containing compound was lanthanum ammonium nitrate. Later he found that molybdenum (sodium or ammonium molybdates) and a boron compound (ammonium diborate or ammonium pentaborate) were also effective in reducing coke formation (Forester, 1991).

Reid and Fields (1992) described a process which includes addition of a combination of a boron compound and a dihydroxybenzene compound to the hydrocarbon feed. The boron compounds included ammonium borate, ammonium diborate, ammonium pentaborate, iron oxide and sodium borate. The dihydroxybenzene compounds included hydroquinone,

resorcinol, catechol, 1-2-naphthaquinone and 4-ter-butyl resorcinol. The total amount of the compounds added was from 1 to 2500 ppm per million parts of feedstock.

Gandman and Hong (1994) patented a process which included the addition of a mixture of a group 1A metal salt, group 2A metal salt and a boron acid or salt to the feedstock. The group 1A metal salt was potassium acetate, potassium metaborate, potassium metasilicate, potassium carbonate, potassium silicotungstate, potassium nitrate or mixtures thereof. The group 2A metal salt was calcium acetate, magnesium acetate, barium acetate, calcium, magnesium and barium salts of alkanolic acids. The boron acid or salt was ortho, meta or tetraboric acid or polyboric acid or ammonium borate.

In a related study, Haga et al. (1990) compared the activities of a variety of binary and ternary catalysts for carbon gasification. They found that some composite catalysts such as sodium and potassium salts, sodium and iron salts, calcium and iron salts, sodium, iron and calcium salts showed higher activities than the individual constituents.

Although considerable work has been reported on the thermal cracking of hydrocarbons, the quantitative data available on the reduction of coke deposition during pyrolysis operation is limited.

Chapter 3

EXPERIMENTAL DETAILS

3.1 Experimental Apparatus

The pyrolysis runs were conducted in a tubular reactor. The schematic diagram of the experimental set up is shown in Figure 1. For ethane pyrolysis, ethane (Matheson Gas Products Inc., USA) flow was metered and preheated to 750K. The temperature in the preheater was controlled by a PI controller (Model IT 401-D-2, Indotherm Instruments, Thane). Water (with or without additive) was fed using a syringe pump (Model 351, Sage Instruments, USA) and mixed with the preheated ethane just before the inlet of the reactor.

The preheated gas entered the tubular reactor. The reactor was a 800 mm length of Inconel tube (i.d. : 4.5 mm; o.d. : 6.0 mm). The reactor was heated in a three zone furnace (Mahendra Scientific Instruments, Kanpur), controlled by an on-off controller. The inlet and outlet of the furnace were insulated by using refractory wool. In order to quench the reaction, the furnace effluent was rapidly cooled in a glass condenser using ice-cold water. In case of naphtha cracking, some portion of the feed was obtained as condensate liquid, which was collected in a separating funnel. Water was separated from the product liquid. The non-condensable gas was passed through a pair of sampling valves for gas analysis, then through a gas flow meter and finally vented to the atmosphere. In order to analyze the

carbon deposited, a bypass line was made just after the reactor outlet. While analyzing the product gas, the bypass line was kept closed.

Nitrogen, which was used as an internal standard in the subsequent chromatographic analysis, was mixed with the reactor effluent just after the liquid product collector. The flow of nitrogen was metered and controlled by means of a mass flow controller (MKS Instruments Inc., USA). In some runs, ethane was diluted with both nitrogen and water. Provision was made to dilute ethane with nitrogen before the preheater. The mixed gases passed through the preheater and were then mixed with the water fed through the syringe pump.

When naphtha was used a feedstock, naphtha and water were taken in graduated burettes and pumped by metering pumps. The naphtha flow rate could be varied from 0 to 0.6 cc/min. while the water flow rate could be adjusted in the range of 0 to 1.8 cc/min. Naphtha and water were passed through two separate 6.3 mm tubes and vaporised in a vaporiser. The temperature in the vaporiser was kept at 523K. The mixed stream was then passed through the preheater.

3.2 Experimental Procedure

An experimental run was initiated by heating the preheater, vaporiser and the reactor to the desired temperature. Initially water containing 50 ppm carbon disulfide was passed for two hours in order to passivate the inner walls of the reactor. Then, the water in the system was flushed by passing nitrogen gas for half an hour. This pretreatment with carbon disulfide was done only during ethane pyrolysis because naphtha contained approximately 80 ppm sulfur. No sulfur compounds were added during the course of a run. After nitrogen flushing,

hydrocarbon and water (with or without additive) were fed from the top of the reactor at the desired flow rate. During the course of the experimental run, the condensate liquid (only in the case of naphtha) and the total gas flow rate were measured at regular intervals. The condensate liquid contained mainly C_5+ compounds. The non-condensable gases containing mainly carbon monoxide, nitrogen and C_1 to C_4 compounds were stored in sampling valves and analyzed by gas chromatography. Due to experimental limitations, hydrogen was not analyzed in this study.

On completion of a run, which was usually of 1 to 3 hours duration, the system was thoroughly flushed with steam (in case of naphtha) or nitrogen (in case of ethane). Subsequently, the coke deposited on the walls of the reactor was burnt by passing preheated air.

3.3 Measurement of Coke

Since the main aim of the study was to reduce the coke formation, the measurement of coke was done very carefully. After flushing off the product gases with steam or nitrogen, the bypass line was opened and the main line was closed. The air to be passed was first made moisture-free by passing through silica gel. The product gases, after burning of the coke, contained carbon monoxide, carbon dioxide, nitrogen and water vapor. The gases were routed through a catalytic converter, consisting of a packed bed of cupric oxide, heated to 623K. Here the carbon monoxide was converted to carbon dioxide. The exit stream from the converter was passed through four U-tubes kept in series. The first two U-tubes contained silica gel in order to adsorb moisture. The next two U-tubes contained two separate portions

of Carbosorb (sodalime-asbestos) and silica gel. Carbon dioxide was adsorbed in Carbosorb. Due to the reaction of Carbosorb with carbon dioxide, water was produced which was adsorbed in silica gel. Initial weights of the U-tubes was measured earlier. From the change in the weights, the amounts of carbon deposited was calculated. To check whether carbon monoxide is fully converted to carbon dioxide, a sampling valve was placed just after the packed bed of cupric oxide.

3.4 Gaseous Product Analysis

The product gases, containing C_1 to C_4 hydrocarbons, small quantities of C_5+ compounds, carbon monoxide and carbon dioxide were analyzed in gas chromatographs using three columns, namely Carbosphere, Duropak and Poropak Q. For separation of the gaseous components, two gas chromatographs, namely AIMIL-NUCON Model 5700 chromatograph equipped with thermal conductivity detector (TCD) and the CIC chromatograph (Model 85 PRO, Chromatograph Instrument Co., Baroda) provided with flame ionisation detector (FID), were used. An electronic recording integrator (Model 3390A, Hewlett-Packard, USA) was used to record the peak areas. A 3.0 mm diameter, 1.83 m long Carbosphere column was used to separate nitrogen, carbon monoxide, methane and carbon dioxide by using TCD. In the TCD, hydrogen was used as the carrier gas and passed at a flow rate of 30 cc/min. The bridge current was 100 mA. The injector, oven and detector temperatures were kept at 333K, 323K and 333K respectively. In the Duropak column, C_1 to C_4 and some C_5+ compounds were separated by using FID. In this case, nitrogen was the carrier gas. The Duropak column was 3.0 mm diameter and 3.0 m long. The oven and the injector temperatures were 313K and

323K respectively. In the Duopak column, ethylene and ethane could not be separated and a combined peak was obtained. To separate ethane and ethylene, a Poropak Q column (3.0 mm i.d., 1.83 m long) was used. The carrier gas and the other operating conditions were the same as for the Duopak column.

For calculating the flow rates of carbon oxides (CO and CO₂), nitrogen was used as the internal standard. From the separation on the Carbosphere column, the peak area ratios of methane to nitrogen and carbon monoxide to nitrogen were calculated. Knowing the calibration factors on this column and the flow rate of nitrogen, the mass flow rates of the carbon oxides could be calculated. The yields of the hydrocarbon products were calculated from the separation on the Poropak Q and Duopak column.

3.5 Liquid Product Analysis

The liquid products were obtained only during naphtha pyrolysis and not with ethane cracking. The liquid products were analyzed on a capillary column (Petrocol DH column) using an FID. The capillary column was 0.25 mm diameter and 100 m long. The split ratio was 1:50. The oven temperature was kept at 333K for a period of 15 mins. and then increased to the final temperature of 423K at the rate of 2K/min. The injector and the detector temperatures were 423K and 493K respectively. The internal standard was 2,2,4-trimethyl pentane (iso-octane). Based on the amount of this compound, the amounts of the liquid products were calculated.

Chapter 4

RESULTS AND DISCUSSION

To study the effect of the anticoking agents on naphtha or ethane pyrolysis, experimental runs with and without additives were conducted. The different anticoking agents were compared under identical conditions. Straight-run naphtha was obtained from Duncan Fertilizer Co., Kanpur where as ethane (minimum purity: 99.0%) was supplied by Matheson Gas Products Inc., USA. For ethane pyrolysis, steam or steam and nitrogen were used as the inert diluent. The dilution ratio was either 0.5 mol steam/ mol ethane (0.3 kg/kg) or (0.5 mol steam + 0.5 mol nitrogen)/ mol ethane. The set temperature was either 1073K or 1103K. The details of the operating conditions for the different runs are shown in Table 4.1. The space times given in Table 4.1 were calculated using the pseudoisothermal approach based on the equivalent reactor volume approach (van Damme et al., 1981; Kumar and Kunzru, 1985). To calculate the equivalent reactor volume, the activation energy for ethane pyrolysis was taken to be 254 MJ/kmol (Froment et al., 1976). Due to the entrance and exit heat losses, there were significant axial temperature gradients in the reactor (refer Figure 2), and the temperature mentioned for of a run refers to the set temperature. It should be noted that in all

Table 4.1 Operating Conditions for Ethane Pyrolysis Runs

parameters	values		
	set 1	set 2	set 3
ethane flow rate, mol/min	1.1×10^{-2}	4.0×10^{-3}	4.0×10^{-3}
steam flow rate, mol/min	5.5×10^{-3}	2.0×10^{-3}	2.0×10^{-3}
nitrogen flow rate, mol/min	-	2.0×10^{-3}	2.0×10^{-3}
reaction temperature, K	1073	1073	1103
steam + nitrogen to ethane molar ratio (δ), mol/mol	0.5	1.0	1.0
space time, s	0.42	0.72	0.72

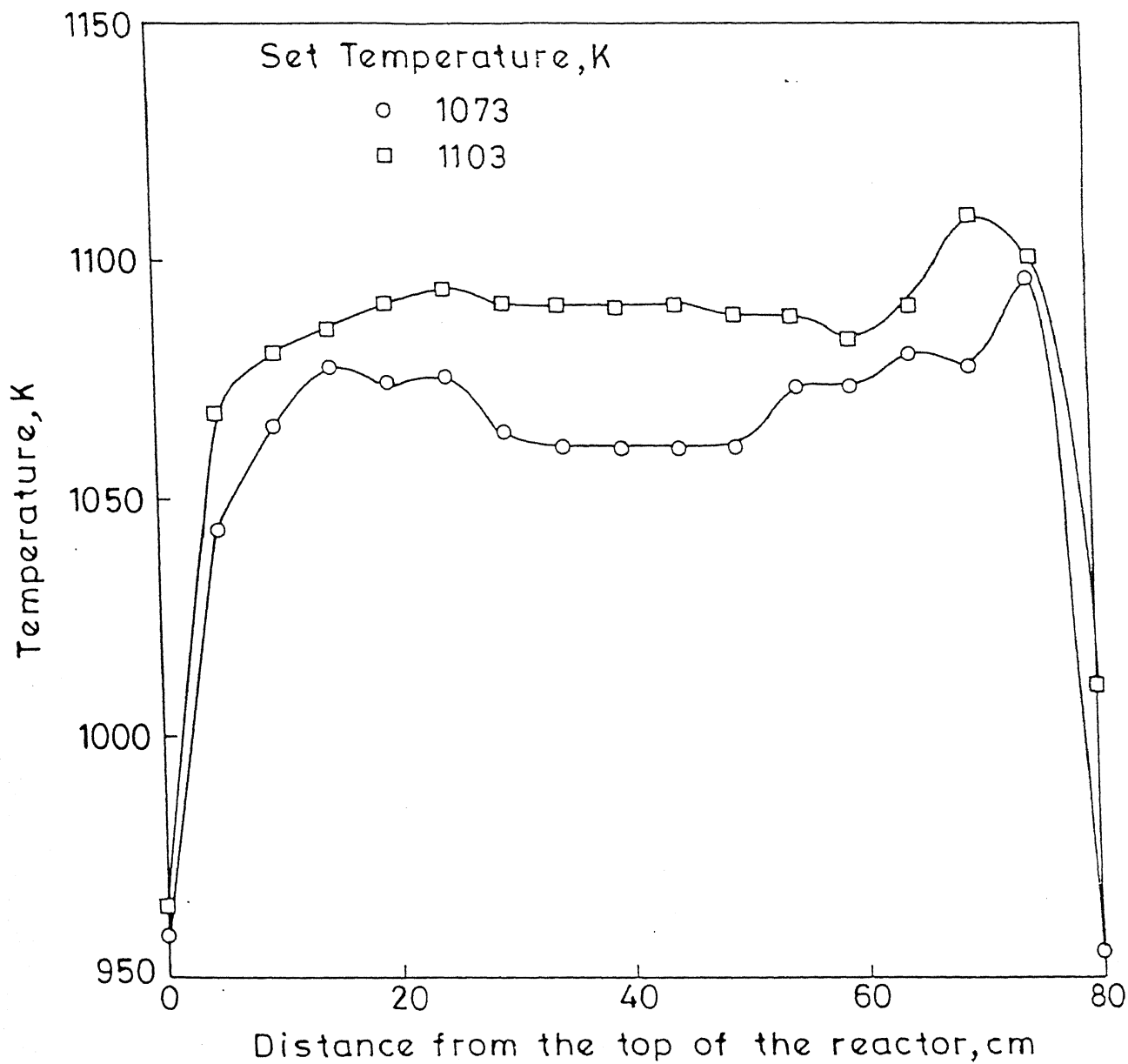


Figure 2 Axial Temperature Profiles in the Tubular Reactor

the runs, the mass of carbon deposited, rather than the mass of coke, has been reported. This was necessary because the moisture present in the connecting lines resulted in unusually high values of the hydrogen content of the coke, which is typically around 8-10% of the coke.

4.1 Pyrolysis of Ethane

4.1.1. Conversion and Product Yields

For most of the runs, the conditions shown in set 1 of Table 4.1 were maintained. The products obtained were methane, ethylene, acetylene, propylene, 1,3-butadiene and carbon monoxide. The product yields at different run times are shown in Table 4.2. At these conditions, the ethane conversion was approximately 70%. As shown in Figures 3 to 5, there was no significant effect of run time either on the conversion or the product yields. Ethylene was the main product and constituted approximately 60 wt.% of the feed. These product yields were in good agreement with the yields reported by Froment et al. (1976). At a ethane conversion of 60%, they reported the yields of ethylene, methane, propylene and 1,3-butadiene to be 50.0, 4.0, 1.1 and 1.1 wt.% feed, respectively. At a temperature of 1073K, Sundaram et al. (1981) have reported the first order rate constant for ethane pyrolysis to be 2.5 s^{-1} . Using an expansion factor of 2.0, the calculated conversion for a space time of 0.42s is 58.7%, compared to the experimental value of 70%.

Experimental runs were also conducted at 1073K and 1103K. The dilution ratio and space time were kept as 1.0 mol/mol and 0.72s respectively. The ethane conversion was 83% at 1073K and 86.6% at 1103K. The ethylene yields were around 60% for both cases.

Table 4.2 Effect of Run Time on Product Yields, Conversion and Carbon Deposition during Ethane Pyrolysis (no Additive)

$T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$

Product yields, wt.% feed	Run time, h		
	1	1.5	2.5
carbon monoxide	1.4	2.2	1.7
carbon dioxide	-	-	-
methane	2.77	2.66	2.68
ethylene	59.61	58.52	60.2
acetylene	tr	tr	0.15
propylene	1.07	1.04	1.01
n-butane	-	-	-
1,3-butadiene	1.31	1.25	1.25
conversion, wt.% feed	70.2	70.49	70.64
carbon deposited, wt.% of feed	0.56	0.45	0.29
carbon deposited, gm	0.11	0.13	0.15

tr : trace

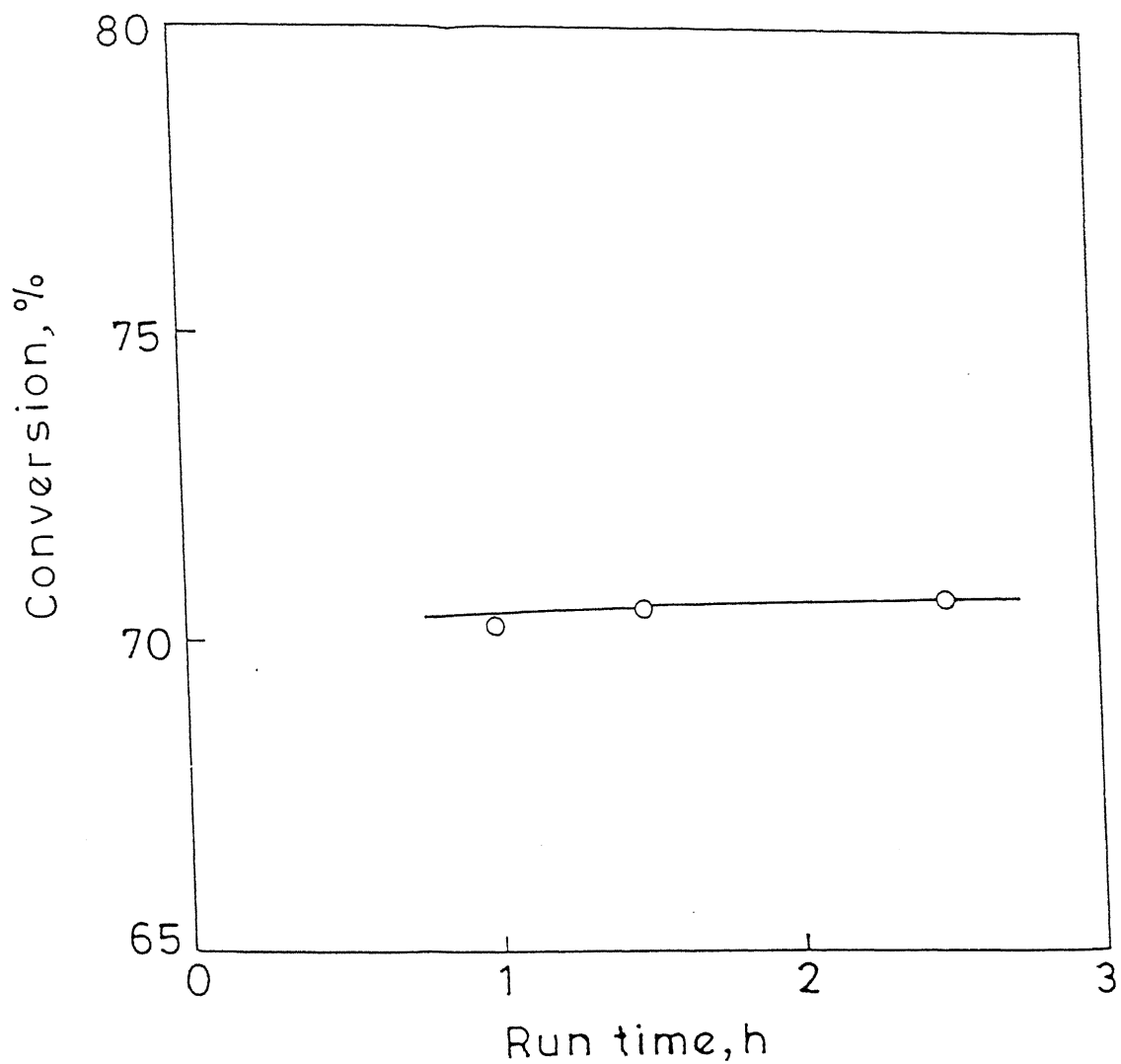


Figure 3 Effect of Run Time on Conversion for Ethane Pyrolysis runs

($T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$)

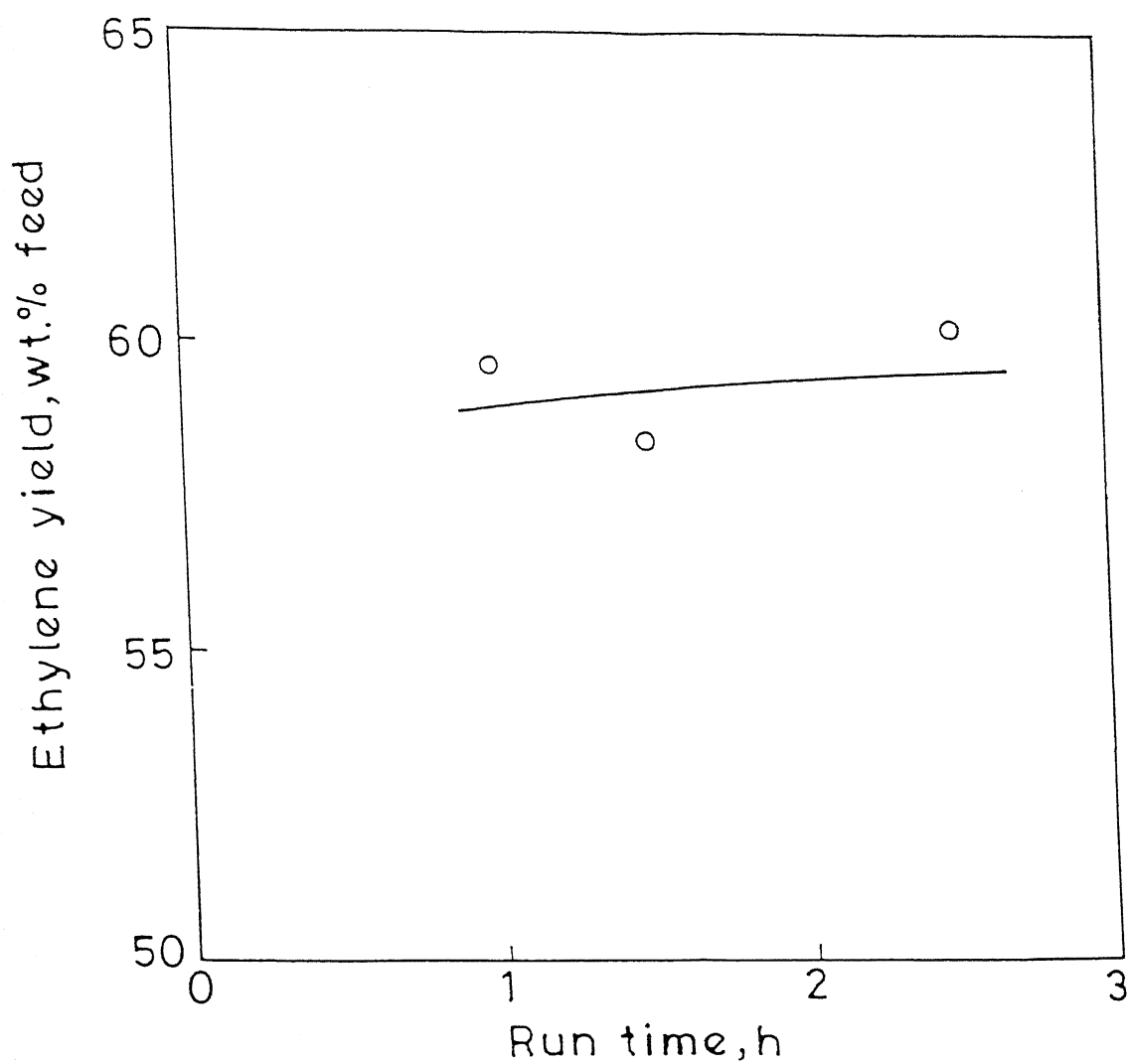


Figure 4 Effect of Run Time on Ethylene Yield during Ethane Pyrolysis

($T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$)

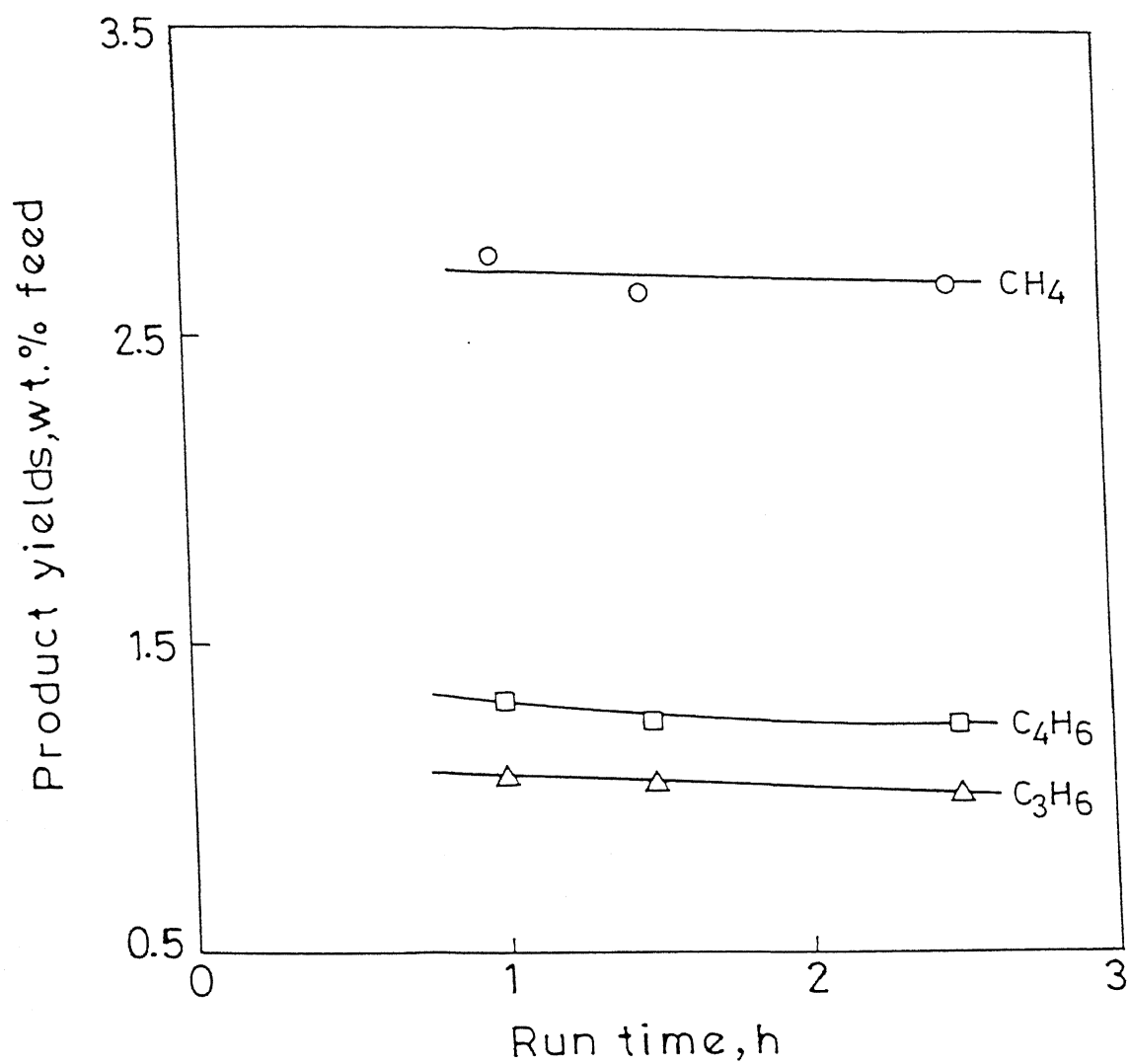


Figure 4.5 Effect of Run Time on Methane, Propylene and 1,3-Butadiene Yields during Ethane Pyrolysis
($T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$)

4.1.2. Carbon Deposition

Due to the type of reactor used, the carbon deposited could not be measured continuously and only the total carbon deposited at 1073K and a steam dilution of 0.5 mol/mol is given in Table 4.2. The carbon deposited varied from 0.56 to 0.29 wt.% feed. The variation of rate of carbon formation with run time is shown in Figure 6. From the figure, it is observed that the rate of carbon deposition was high initially, then gradually decreases with run time and approaches an asymptotic value. This is due to the formation of a layer of coke on the surface of the reactor, which inhibits the catalytic activity of the metals. The initial rate of coking was $0.01 \text{ kg/m}^2\text{h}$, gradually decreased to $0.004 \text{ kg/m}^2\text{h}$ and finally became $0.002 \text{ kg/m}^2\text{h}$. Using a mixed flow reactor and a dilution ratio of 1.0 mol nitrogen/mol ethane, Sundaram et al. (1981) reported the asymptotic coking rate to be in the range of 0.004 to $0.01 \text{ kg/m}^2\text{h}$. Valenyi et al. (1991) studied the coke formation during ethane pyrolysis in a tubular reactor. Using pure ethane as the feed, the coking rates on an Inconel 600 reactor varied from 0.005 to $0.05 \text{ kg/m}^2\text{h}$. The maximum temperature in the reactor was 1198K.

To study the effect of temperature on carbon formation, experimental runs were conducted at 1073K and 1103K at otherwise identical conditions. the variation of the total carbon deposition (at different temperatures) with run time is shown in Figure 7. As expected, the carbon deposition was higher at the higher temperatures. The value of the activation energy for carbon deposition was estimated at these two temperatures and was found to be approximately 268 MJ/kmol reported by Albright and McConnell (1978).

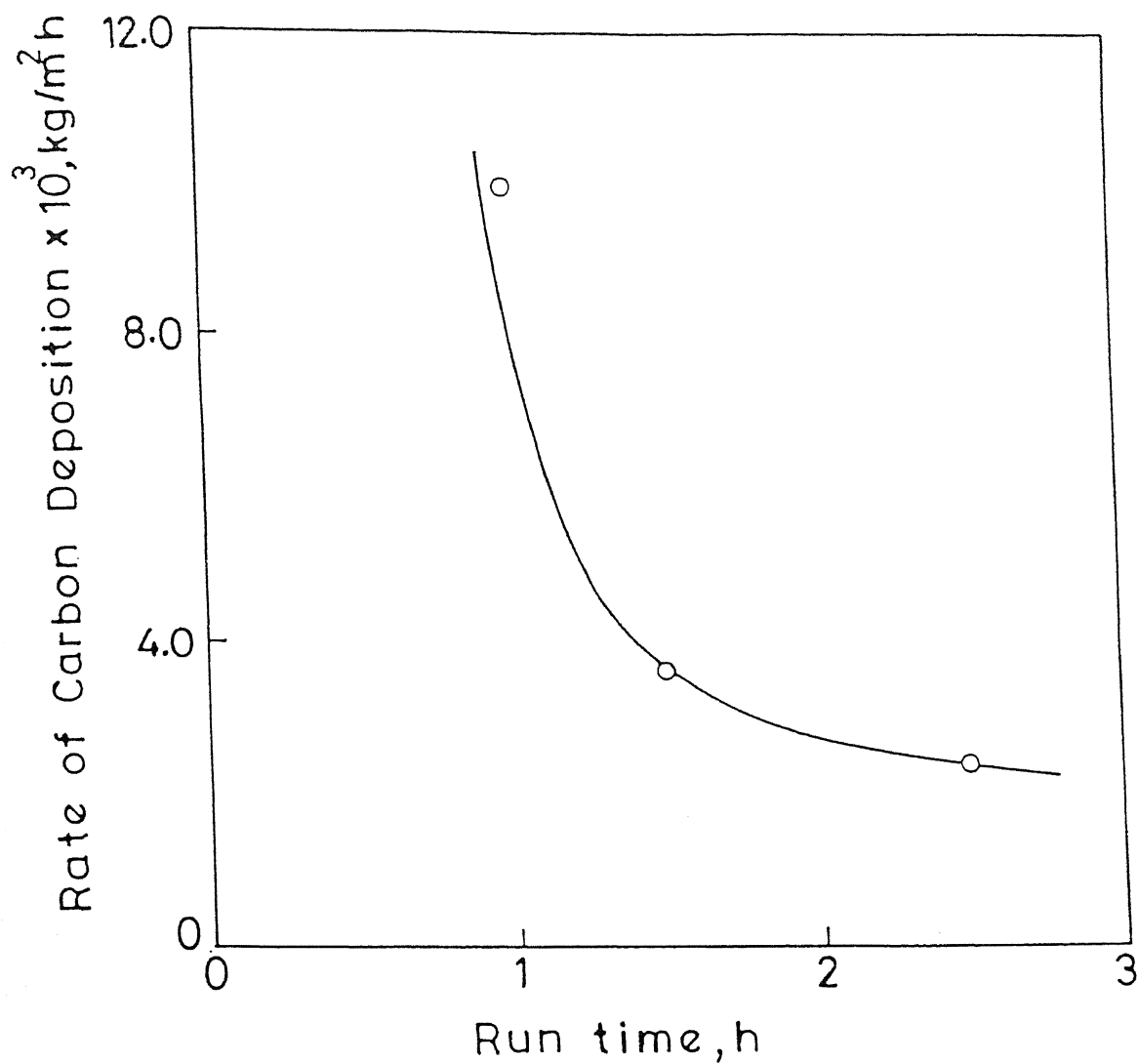


Figure 6 Effect of Run Time on Rate of Carbon Deposition for Ethane

Pyrolysis

($T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$)

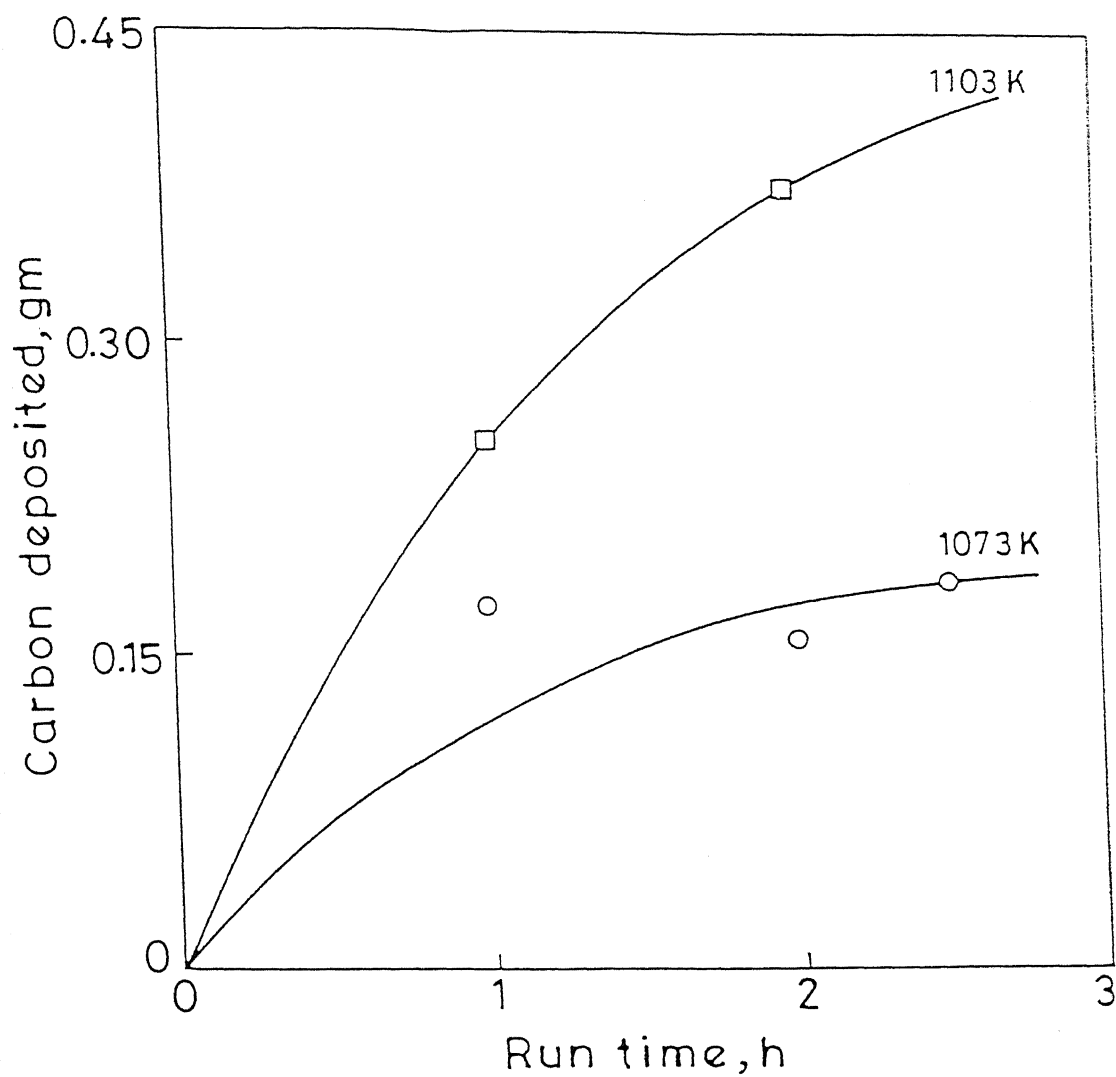


Figure 7 Effect of Temperature on Carbon Deposition at Different Run Times for Ethane Pyrolysis
($\delta = 1.0 \text{ mol/mol}$, $\tau = 0.72 \text{ s}$)

4.2 Effect of Additives on Conversion, Product Yields and Carbon Deposition

4.2.1. Effect of Potassium Carbonate

Potassium carbonate is known to be a catalyst for gasification and its effect on the in situ gasification of coke during ethane pyrolysis at 1073K was investigated by dissolving potassium carbonate in the feed water used in the pyrolysis runs. The concentration of potassium (as potassium carbonate) in the feed water was varied from 50 to 150 ppm. The amount of carbon deposited with run time is shown in Figure 8. For the sake of comparison, the carbon deposited with no additive is also shown in this figure. As can be seen from Figure 8, the amount of carbon deposited after 3 hours was reduced by 88%. Using 150 ppm potassium, the carbon deposited (as wt.% feed) varied from 0.07 at a run time of 1 hour to 0.03 at a run time of 3 hours. No quantitative data is available in the published literature regarding the reduction in the carbon deposition by using potassium carbonate. In a related study, Mandal and Kunzru (1986) measured the rate of coke deposition on potassium carbonate coated steel surfaces. For a potassium carbonate concentration of $5.057 \times 10^{-3} \text{ kg/m}^2$, no measurable coke was formed even after 3 hours of continuous operation.

The product yields obtained in the presence of potassium carbonate are given in Table 4.3. A comparison of Tables 4.2 and 4.3 shows that the overall ethane conversion as well as the yields of methane, propylene and 1,3-butadiene were not affected by the addition of

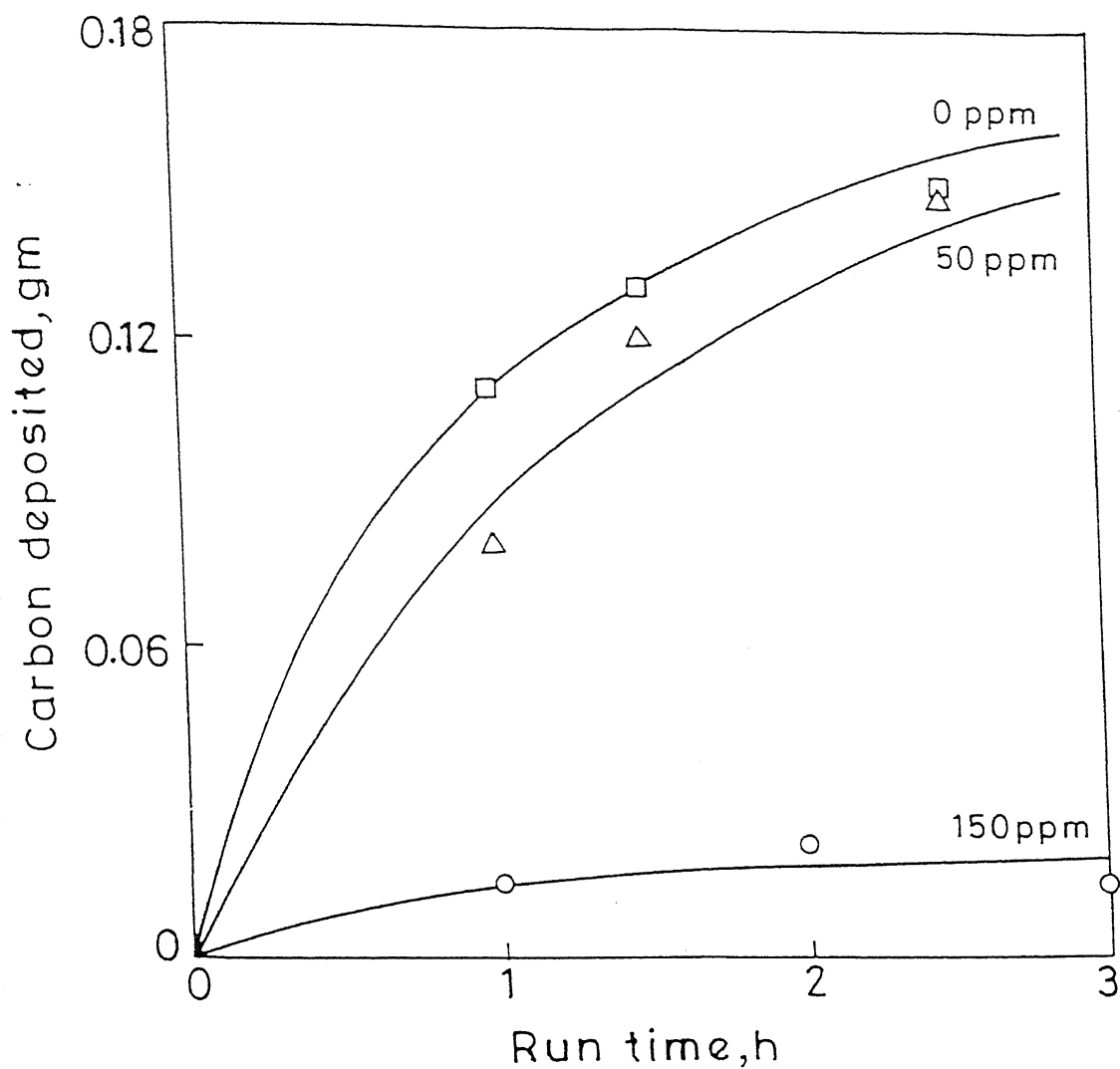


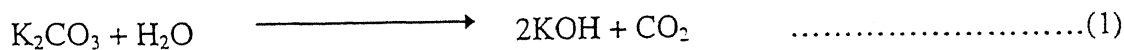
Figure 8 Effect of Potassium Carbonate on Carbon Deposition for Ethane Pyrolysis

($T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$)

potassium carbonate. However, the ethylene yields were decreased due to potassium carbonate addition. On the other hand, the carbon oxide yields were significantly higher with potassium carbonate. In the blank runs, no carbon dioxide was detected, whereas appreciable amounts of carbon dioxide were present when potassium carbonate was added. Calculations showed that the carbon gasification reaction alone could not account for the increase in the carbon oxide yields. It should be emphasized that the increase in carbon oxide yields due to the addition of potassium carbonate is not only due to enhanced coke-steam reactions but also due to the increased rates of the hydrocarbon-steam reactions. Potassium carbonate can also catalyze steam reforming reactions (Pant and Kunzru, 1997). The decrease in the ethylene yields (refer Table 4.3) suggests that the reaction of ethylene with steam in the presence of potassium carbonate is not insignificant, and the product distribution indicates that carbon oxides are formed through this reaction also.

Various mechanisms have been proposed to explain the catalytic effect of potassium carbonate during carbon gasification (Moulijn and Kapteijn, 1986; Huttinger and Minges, 1986). Majority of these mechanisms are based on an oxidation-reduction cycle at the potassium carbonate interphase.

Huttinger and Minges (1986) suggested that potassium carbonate is converted to potassium hydroxide in the presence of steam.



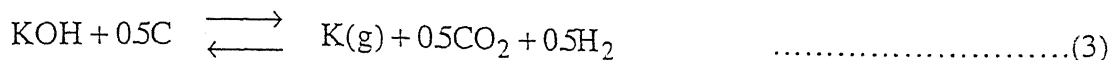
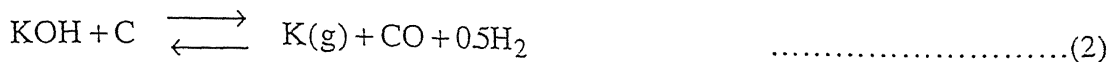
The potassium hydroxide reacts with carbon and this reaction is probably a direct carbothermic reaction.

Table 4.3 Effect of Potassium Carbonate on Product Yields, Conversion and Carbon Deposition for Ethane Pyrolysis

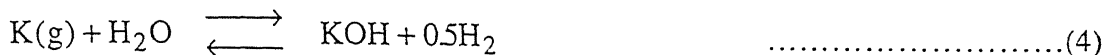
$T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$

product yields wt. % feed	50 ppm K (as K_2CO_3)		150 ppm K (as K_2CO_3)		
	run time, h		run time, h		
	1	1.5	1	2	3
carbon monoxide	a	5.9	13.4	a	11.0
carbon dioxide	a	2.2	7.3	a	5.66
methane	a	2.5	2.77	a	2.43
ethylene	a	57.8	53.1	a	52.4
acetylene	a	a	-	a	-
propylene	a	1.07	0.74	a	0.83
n-butane	a	0.1	-	a	-
1,3-butadiene	a	1.1	0.71	a	0.8
conversion wt. %	a	71.09	70.2	a	67.9
carbon deposited wt. % feed	0.4	0.38	0.07	0.05	0.03
carbon deposited, gm	0.081	0.116	0.014	0.022	0.015

a : not measured



These reactions occur at the potassium-carbon interphase and hydrolysis reaction (3) takes place at the interphase with water vapor.



This potassium may form potassium oxide in contact with potassium hydroxide



Besides potassium oxide, other potassium oxygen compounds are also possible. These potassium oxygen compounds present at the potassium carbon interphase under steady state conditions may be written as K_xO_y^- ($x > y$). This non-stoichiometric potassium oxygen compound, K_xO_y^- is primarily oxidized by the reaction with water vapor and a non-stoichiometric potassium oxygen compound K_xO_y^+ ($y > x$) is formed. This K_xO_y^+ reacts with the carbon at the surface to form mainly carbon monoxide and reduces to K_xO_y^- . Again, this carbon monoxide take up more oxygen from K_xO_y^+ to form carbon dioxide.



The reaction scheme for the gasification reactions in the presence of potassium carbonate is shown in Figure 9. The overall reactions for gasification can be written as

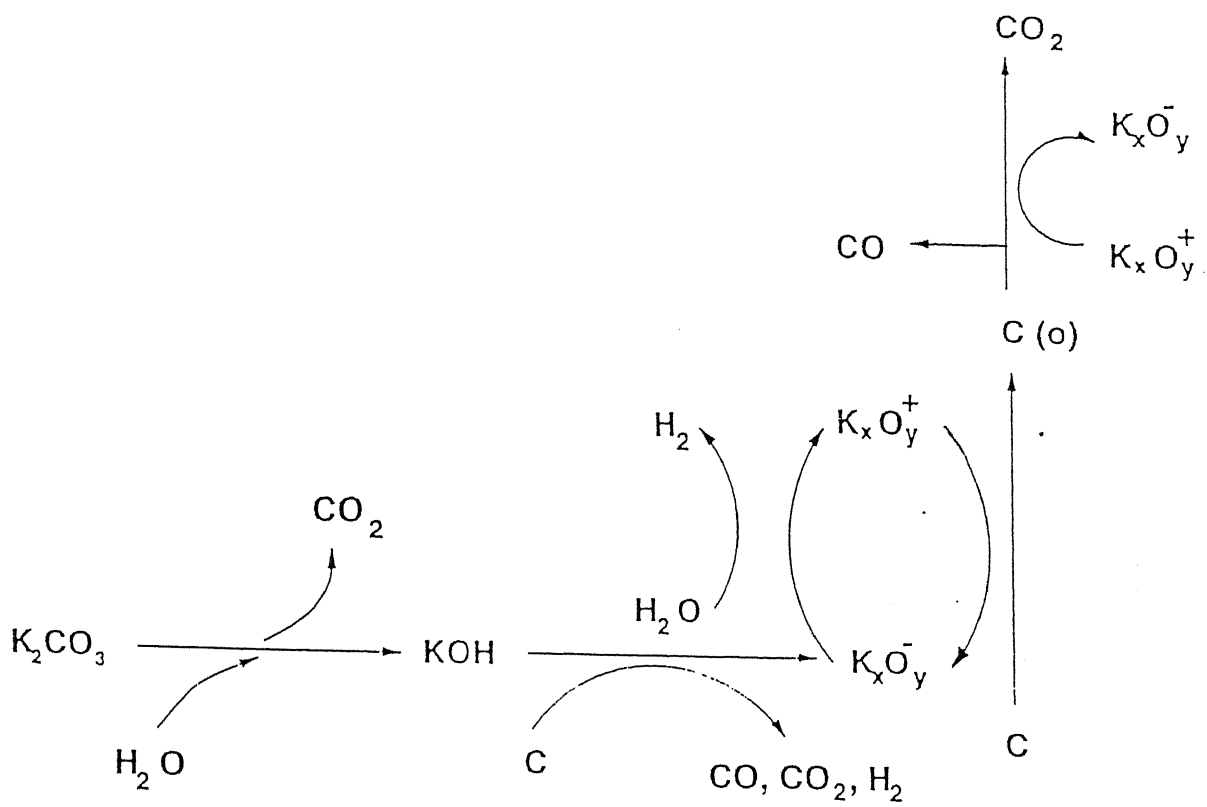
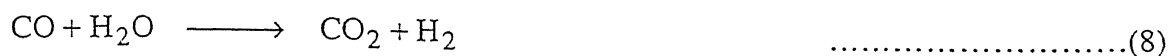


Figure 9 Reaction Scheme of Gasification Reactions



The mechanism of gasification reactions, catalyzed by potassium carbonate, explains the high yield of carbon dioxide during the ethane pyrolysis in presence of potassium carbonate.

4.2.2 Effect of Other Additives

Besides potassium carbonate, potassium salts such as potassium hydroxide, potassium dihydrogen phosphate and a potassium salt of a weak acid (KA) were also tested for their effectiveness as coke inhibitors.

The proposed mechanism of the catalytic effect of potassium carbonate on coke gasification, as discussed above, suggests that potassium carbonate is first converted to potassium hydroxide and this then takes part in the carbon gasification reaction. Keeping this in mind, potassium hydroxide was tried as an additive. The concentration of potassium hydroxide used was 150 ppm and the run time was 1 hour. The results are given in Table 4.4. As shown in Table 4.4, the carbon deposited was higher (0.19 gm) as compared to a run with no additive (0.11 gm). The ethane conversion as well as the yields of methane, ethylene, propylene and 1,3-butadiene were much lower than that in the blank run whereas the yields of carbon oxides were higher. The ethylene yield was 52% as compared to 60% obtained in a run with no additive. The product yields suggest that potassium hydroxide catalyzes the steam reforming of ethylene but increases the coke deposition. The reason for the adverse effect of potassium hydroxide on the coke deposition is not clear.

Table 4.4 Effect of Potassium Hydroxide and Potassium Dihydrogen Phosphate on Product Yields, Conversion and Carbon Deposition for Ethane Pyrolysis

$T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$, run time = 1 h

Product Yields, wt.% feed	150 ppm K (as KOH)	50 ppm K (as KH_2PO_4)
carbon monoxide	2.44	1.9
carbon dioxide	1.55	-
methane	1.85	2.09
ethylene	52.19	55.89
propylene	0.77	0.94
n-butane	0.15	0.13
1,3-butadiene	0.79	0.95
conversion, wt. %	61.4	66.02
carbon deposited, wt. % feed	0.96	1.6
carbon deposited, gm	0.19	0.32

Phosphorus compounds can inhibit coke formation (Naberezhnova et al., 1983; Boone, 1983; Vaish and Kunzru, 1989; Das et al., 1992; Taylor and Allen, 1994). Therefore, a compound of potassium and phosphorus was chosen as an additive to reduce carbon deposition during the pyrolysis of ethane. 50 ppm of potassium as potassium dihydrogen phosphate was used and the results are shown in Table 4.4. The amount of carbon deposited was 0.32 gm which was much higher than that in the blank run (0.11 gm). The ethylene yield (55.9%) was lower than that in the blank runs (60%). There was no significant increase in carbon monoxide yield. No carbon dioxide was detected with this additive, which suggests that this additive did not promote carbon gasification. No published results are available regarding the effect of potassium hydroxide or potassium dihydrogen phosphate on coke gasification during hydrocarbon pyrolysis.

To see whether the anion has an effect on the coke deposition and product yields, a potassium salt with a different anion was tested. This was a salt of a weak acid. This salt was dissolved in feed water to give a concentration of 150 ppm potassium in water. The run time was varied to observe its effects on the ethane conversion, product yields and the carbon deposition and the results are shown in Table 4.5. As compared to a run with no additive, the amount of carbon deposited was significantly lower. For a run time of 1 hour, the reduction in carbon deposition was more than that obtained with potassium carbonate; however at longer run times, the reduction using KA was approximately the same as that obtained using 150 ppm potassium as potassium carbonate (refer Table 4.3). There was no significant effect of run time either on the conversion or the product yields. The ethylene yield (wt.% feed) as well as the conversion were slightly lower than the blank run (refer Table 4.2), but the selectivities

Table 4.5 Effect of KA on Product Yields, Conversion and Carbon Deposition during Ethane Pyrolysis at Different Run Times

$T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$

Potassium content of water : 150 ppm

Product yields, wt.% feed	Run time, h		
	1	1.5	2.5
carbon monoxide	1.94	2.8	2.47
carbon dioxide	1.07	2.0	2.5
methane	1.7	1.82	1.89
ethylene	55.47	55.65	56.12
acetylene	tr	tr	tr
propylene	0.83	0.86	0.83
n-butane	0.13	0.12	0.12
1,3-butadiene	0.95	0.98	0.95
conversion, wt.%	64.47	65.63	66.02
carbon deposited, wt.% feed	0.03	0.08	0.04
carbon deposited, gm	0.006	0.023	0.022

of ethylene (kg ethylene produced/kg ethane cracked) were nearly the same. Using KA, the selectivity of ethylene was 0.855 kg ethylene/kg ethane cracked compared to a value of 0.857 kg ethylene/kg ethane cracked for a run with no addition. The yields of carbon oxides were higher than the blank run but significantly lower than that obtained with potassium carbonate. The lower carbon oxides and higher ethylene yields, as compared to potassium carbonate runs, implies that the steam reforming of ethylene was not significantly enhanced by the addition of KA.

Besides potassium compounds, a calcium compound (calcium acetate) was also used as an additive. The alkaline earth metals especially calcium acetate has been reported to reduce coke deposition (Forester, 1989; Gandman and Hong, 1994). The concentration of calcium as calcium acetate in the feed water was varied from 50 to 150 ppm, and the effect of calcium acetate on the conversion, product yields and the carbon deposition is shown in Table 4.6. As compared to a run with no additives, with calcium acetate, the carbon deposition was significantly higher whereas the ethane conversion and the yields of methane, propylene and 1,3-butadiene were slightly lower. On the other hand, the ethylene yield was approximately the same and the yields of carbon oxides lower than that for a blank run. These results (lower carbon oxides; higher carbon yields) imply that the salt does not catalyze either the coke-steam reactions or the steam-hydrocarbon reforming reactions. To further check the effect of calcium acetate on the coke deposition, prior to a run, the walls of the reactor were coated with a layer of calcium acetate by passing water containing calcium acetate for 2 hours, with the reactor maintained at 1073K. Subsequently, the ethane feed was started. However, the reactor had to be shut down after 20 minutes due to high pressure drop caused by excessive

Table 4.6 Effect of Calcium Acetate on Product Yields, Conversion and Carbon Deposition during Ethane Pyrolysis

$T = 1073\text{K}$, $\delta = 0.5 \text{ mol/mol}$, $\tau = 0.42 \text{ s}$, run time = 2 h

product yields, wt.% feed	50 ppm Ca as $\text{Ca}(\text{CH}_3\text{COO})_2$	150 ppm Ca as $\text{Ca}(\text{CH}_3\text{COO})_2$
carbon monoxide	0.77	tr
carbon dioxide	-	-
methane	2.12	1.97
ethylene	59.61	59.31
acetylene	tr	0.12
propylene	0.8	0.87
n-butane	tr	0.09
1,3-butadiene	0.89	1.15
conversion, wt.%	68.17	68.4
carbon deposited, wt.% feed	0.58	1.06
carbon deposited, gm	0.23	0.43

coke formation. Thus, the experiments with calcium acetate do not support the results of Forester (1989) or Gandman and Hong (1994).

In summary, of all the additives tested (potassium carbonate, potassium hydroxide, potassium dihydrogen phosphate and KA), only potassium carbonate and KA were equally effective in reducing the carbon deposition during ethane pyrolysis. Using a concentration of 150 ppm potassium in the feed water, a reduction of 82 to 88% could be achieved. A disadvantage of potassium carbonate is significantly higher yields of carbon oxides and consequently lower yields of ethylene. On the other hand, with KA the steam reforming of ethylene is not significantly enhanced and therefore the ethylene yields are higher and the carbon oxides lower.

4.3 Effect of Additives on Pyrolysis of Naphtha

Some preliminary data were obtained on the effect of two potassium salts (potassium carbonate and potassium peroxodisulfate) on the coke deposition during naphtha pyrolysis. Naphtha pyrolysis was carried out at 1073K. The dilution ratio and space time were kept as 1.05 kg/kg and 0.26 s respectively. The details of the operating conditions are shown in Table 4.7. The sulfur content of the naphtha feed was 323K to 433K, the density 705 kg/m³ and the average molecular weight 90. The detailed characteristics of the naphtha feed are given in Table 4.8. Pyrolysis operation was carried out under identical conditions with or without additives. In each case, the run time was 3 hours.

Table 4.7 Operating Conditions for Naphtha Pyrolysis Runs

parameters	values
naphtha flow rate, g/min	0.39
steam flow rate, g/min	0.4
reaction temperature, K	1073
steam to naphtha weight ratio (δ), kg/kg	1.05
space time (τ), s	0.26

Table 4.8 Characteristics of Naphtha Feed

Properties:

(i) Density (298K) 705 kg/m³

(ii) ASTM Distillation K

IBP	323
5%	337
10%	340
50%	370
90%	403
95%	411
FBP	433

(iii) Sulfur content 80 ppm

4.3.1 Product Yields and Carbon Deposition during Naphtha Pyrolysis (No Additive)

The main products during naphtha pyrolysis were methane, ethylene, propylene and 1,3-butadiene. The detailed product yields are shown in Table 4.9. The total wt.% of cracked gas was 75.49% whereas the yields of methane, ethylene, propylene and butadiene yields were 13.97, 29.82, 17.3 and 7.86 wt.% feed, respectively. The amount of carbon deposited in 3 hours was 0.39 gm and yield of coke was 0.5 wt.% of the feed. These yields are in good agreement with the published data. Bajus et al. (1980), during the steam cracking of naphtha at 1073K, using a dilution ratio of 1.0 kg steam/kg naphtha and space time of 0.26 s, reported the wt.% of cracked gas to be 85.27% and the yields of methane, ethylene, propylene and 1,3-butadiene to be 14.61, 29.09, 17.0 and 4.3 wt.% feed respectively. The carbon monoxide comprised 0.94 wt.% of feed whereas no carbon dioxide was detected.

Potassium carbonate and potassium peroxodisulfate were added at different concentrations to determine their effect on coke deposition. Potassium carbonate is known to gasify the coke during the pyrolysis of hydrocarbons (Mandal and Kunzru, 1986; Bahadur et al., 1987). The concentration of potassium carbonate in the feed water was adjusted such that the potassium content of water varied from 300 to 600 ppm. The product yields and carbon deposition obtained in the presence of potassium carbonate are also shown in Table 4.9. As in the case of ethane pyrolysis, the coke formation was significantly reduced due to enhanced coke-steam reaction. However, for the same reduction in coke, a high concentration of potassium is required for naphtha. The amount of carbon deposited decreased with increasing concentration of potassium. The carbon deposited was as low as 0.07 gm with 600 ppm of

Table 4.9 Effect of Potassium Carbonate of Different Concentrations on Product yields, Conversion and Carbon deposition for Naphtha Pyrolysis

$T = 1073\text{K}$, $\delta = 1.0\text{ kg/kg}$, $\tau = 0.26\text{ s}$, run time = 3 h

product yields, wt.% feed	blank run	300 ppm K (as K_2CO_3)	600 ppm K (as K_2CO_3)
methane	13.97	14.37	16.23
ethylene	29.82	32.24	27.81
ethane	2.28	2.28	2.43
acetylene	0.39	tr	0.57
propane	0.23	tr	0.29
propylene	17.3	14.37	19.73
isobutane	0.2	tr	tr
n-butane	0.16	tr	0.15
1-butene	1.41	1.18	1.02
2-butene+isobutylene+ 1,3-butadiene	7.86	7.11	7.33
Others	1.87	2.73	1.18
wt.% of cracked gas	75.49	74.28	76.76
carbon monoxide	0.94	1.73	2.88
carbon dioxide	tr	2.51	3.92
carbon deposited, wt.% feed	0.5	0.38	0.1
carbon deposited, gm	0.39	0.28	0.07

potassium as potassium carbonate, as compared to 0.39 gm during blank runs. A 82% decrease in carbon deposition was achieved with 600 ppm potassium carbonate. The carbon monoxide as well as carbon dioxide yields increased with increasing potassium concentration. In ethane runs, with 300 ppm potassium as potassium carbonate the carbon monoxide and carbon dioxide yields were 11 to 13.4% and 5.7 to 7.3%, respectively. Compared to these values, the carbon monoxide and carbon dioxide yields for the same concentration of potassium carbonate were 1.73% and 2.51%, respectively. There was no significant effect of potassium on total cracked gas yields. Due to the scatter in data and limited runs, no conclusive statement can be made regarding the effect of potassium carbonate on the methane, ethylene, propylene and 2-butene + isobutylene + 1,3-butadiene yields.

Experimental runs were conducted with 150 to 300 ppm concentration potassium (as potassium peroxodisulfate). Sulfur compounds are known to reduce coke formation (Bajus et al., 1981,1983; Sahu and Kunzru, 1988). Therefore, a salt containing sulfur and potassium was chosen as an additive. The effect of this compound on product yields and coke formation is shown in Table 4.10. It was found to be effective in reducing coke formation. There was a 72% reduction in carbon deposition with 300 ppm of potassium as potassium peroxodisulfate as compared to 28% reduction with the same concentration of potassium as potassium carbonate. There was no significant change in the cracked gas yields. As shown in Table 4.10, with increasing concentration of potassium peroxodisulfate, the yields of carbon oxides showed a maxima. In fact, at a concentration of 300 ppm potassium, only traces of carbon oxides were detected. The yields of carbon oxides were significantly lower than that

Table 4.10 Effect of Potassium Peroxodisulfate on Product Yields, Conversion and Carbon Deposition during Naphtha Pyrolysis

$T = 1073\text{K}$, $\delta = 1.0 \text{ kg/kg}$, $\tau = 0.26 \text{ s}$, run time = 3 h

product yields, wt.% feed	blank run	150 ppm K (as $\text{K}_2\text{S}_2\text{O}_8$)	300 ppm K (as $\text{K}_2\text{S}_2\text{O}_8$)
methane	13.97	15.97	17.96
ethylene	29.82	31.45	29.88
ethane	2.28	2.46	3.24
acetylene	0.39	0.57	0.49
propane	0.23	0.25	0.25
propylene	17.37	18.67	16.44
isobutane	0.2	0.23	tr
n-butane	0.16	tr	tr
1-butene	1.41	0.86	0.78
2-butene+isobutylene+	7.86	6.14	5.77
butadiene			
others	1.87	0.96	1.22
wt.% of cracked gas	75.49	77.56	76.03
carbon monoxide	0.94	1.57	tr
carbon dioxide	tr	1.87	tr
carbon deposited, wt.% feed	0.5	0.35	0.16
carbon deposited, gm	0.39	0.25	0.11

obtained with potassium carbonate (refer Table 4.3). A possible reason for the lower carbon oxide yields with potassium peroxodisulfate could be the presence of sulfur in the system. Although conflicting results have been published regarding the effect of sulfur on the coke deposition during hydrocarbon pyrolysis (Trimm and Turner, 1981; Reyneirs and Froment, 1995), it is well established that sulfur reduces the formation of carbon monoxide (Froment, 1990) by inhibiting the gasification of the steam reforming process, which is mainly responsible for the production of carbon monoxide during pyrolysis. The results suggest that at 150 ppm potassium (as potassium peroxodisulfate), the increased carbon oxide yields are due to the enhanced rate of the coke-steam reaction and at this concentration, the effect of sulfur is not prominent. At high concentration, the effect of sulfur increases and the carbon oxides were significantly reduced.

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of this study, the following conclusions can be made:

- For ethane pyrolysis, the coking rates are initially high and decrease with run time to an asymptotic value.
- Addition of gasifying agents such as potassium carbonate or KA (potassium salt of a weak acid) significantly reduce the coke deposition during ethane pyrolysis. Both are equally effective in reducing the coke deposition.
- Potassium carbonate also catalyzes the ethylene-steam reaction, resulting in significantly lower yields of ethylene and approximately high yields of carbon oxides. On the other hand, the selectivity of ethylene with KA is approximately the same as that for a run with no additive.

- Potassium hydroxide and potassium dihydrogen phosphate have an adverse effect on the coke deposition during ethane pyrolysis.
- Both potassium carbonate and potassium peroxodisulfate are effective coke inhibitors during naphtha pyrolysis. Due to the presence of sulfur, the carbon oxides yields in the presence of potassium peroxodisulfate are significantly lower than that of potassium carbonate.

5.2 Recommendations

- A detailed investigation should be carried out with the potassium salt of weak acid (KA) at different concentrations.
- Search for a proper anticoking agent should be made which will not only gasify the coke but also increase the ethylene yield. Special attention should be given to the carbon monoxide yield as high yields are not desirable.
- Experiments should be carried out with composite salts (salts of alkali metal and alkaline earth metal) as these have been reported in the patent literature to reduce coke deposition.
- The effect of sulfur compounds on the rate of coke deposition should be investigated as there is a controversy whether it reduces or increases the coke deposition.

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